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V. On a new Gaseous Compound of Carbon and Hydrogen. By Edmund Davy, F.R.S. M.R.I.A., &c., Professor of Chemistry to the Royal Dublin Society.

Read 26th June, 1837.

I communicated to a Scientific Meeting of the Royal Dublin Society, and also to the last Meeting of the British Association for the Advancement of Science, held at Bristol in August, 1836, a brief notice of a new gaseous compound of carbon and hydrogen, I had previously obtained; in order to secure my claim to priority of discovery, and with the intention of subsequently submitting to the Royal Irish Academy a fuller and more detailed account of it. Circumstances, which it is unnecessary to mention, have hitherto prevented me from executing this design, which I shall now do myself the honor of carrying into effect.

In attempting to make potassium, on a large scale, in an iron bottle, by what has been called Brunner's method, i. e. by strongly heating a mixture of previously calcined cream of tartar, and about $\frac{1}{14}$ of dry charcoal powder, I failed; and instead of potassium, I obtained only a very limited quantity of a black substance, which choked up a part of the iron tube connected with the iron bottle. This black substance was hastily transferred to a dry bottle, which was then well corked. A small part of it was in powder, but the greater part in little lumps, which though apparently similar to the eye, yet produced different effects in water; for whilst some of those lumps slowly decomposed water, evolving only very minute globules of gas; others decomposed that fluid very rapidly, producing all the gas they would furnish, with nearly the same facility as potassium would have done, under similar circumstances. The gas, thus slowly produced, was on examination found to be hydrogen; whilst the gas rapidly evolved, possessed properties so different from any other known gas, as to entitle it to be

regarded as a new combination. I purpose, at my earliest leisure, to make the black substance to which I have referred, the subject of a separate communication to the Academy, and to confine myself at present chiefly to the properties and composition of the new gas.

MODE OF OBTAINING THE NEW GAS.

The new gas was obtained by the action of pure water, (previously boiled for some time,) on the black substance. It was collected in a tube over water, by nearly filling the tube with dry mercury, putting into it a few lumps of the black substance, pressing the thumb closely to the top of the tube, so as to exclude any air, and inverting the tube in water; then by a slight relaxation of the thumb, the mercury was allowed gradually to descend, and the water coming in contact with the black substance, the gas was readily generated. In cases where the gas was collected over mercury, a few lumps of the black substance were placed at the bottom of a tube, which was held in an oblique position, and cautiously filled with mercury, so as to retain the black substance at or near the bottom of the tube, which, being then inverted in mercury, a little pure water was let up into the tube, when the gas was of course readily produced.

In every instance in which the new gas was collected, whether over water or mercury, some carbonaceous matter (apparently liberated during the generation of the gas) adhered to the sides of the tubes, and surface of the water or mercury; so that previous transfer to another receiver was necessary, before the gas could be used. Sometimes I operated on the new gas over water, at other times over mercury. In the subsequent experiments on its analysis, it was first collected over water in one tube, then transferred to another, which being filled with it, was removed to a mercurial apparatus, and dried first by means of bibulous paper, then let up into a dry receiver, and exposed for some days to the action of chloride of calcium, which had been previously heated to redness. Six grains of the black substance, I found, in one instance, yielded about two cubic inches of the new gas.

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PROPERTIES OF THE NEW GAS.

This gas is colourless, invisible, and possesses the mechanical properties of common air. It is highly inflammable, and when kindled in contact with air, it burns with a bright white flame, apparently denser, and of greater splendour, than that of olefiant gas, under similar circumstances. This may be strikingly shown by making a comparative experiment, and burning equal bulks of olefiant gas, and of the new gas, separately, in a tube;—the former will burn with a bluish flame, the latter with a bright white flame. If the supply of air is limited during the combustion of the new gas, there is a copious deposition of carbon in the form of light flakes. When the new gas was mixed with about six times its volume of air, it exploded, when kindled, producing a white flame and a whistling sound. One measure of the new gas being mixed with about ten measures of air in a tube, and kindled, produced a loud explosion, accompanied by a blue flame, which pervaded nearly the whole length of the tube. One measure of the new gas, and nineteen of air, burned rapidly with a blue flame.

The new gas forms with oxygen, a powerful explosive mixture, especially when the volume of the latter is about three or four times that of the former. In exploding a mixture of this kind in a detonating tube about half an inch in diameter, and nearly one-third of an inch thick, the tube was shattered in pieces by the violence of the shock, though the volume of new gas did not exceed $\frac{5}{100}$ of a cubic inch.

When chlorine is brought in contact with the new gas, instant explosion takes place, accompanied by a large red flame, the deposition of much carbon, and condensation (to a certain extent) of the two gases; and these effects occur in the dark, and are of course quite independent of the action of the sun's rays, or of light.

The new gas is permanent over mercury, and may apparently be kept over this fluid for an indefinite length of time, without undergoing any change. It is slowly absorbed by water, and agitation promotes the effect. I made the following experiment, to determine the quantity of the new gas which water would absorb:—

Experiment.

Thermometer 55° Fah. Barom. 30°.

of a cubic inch of pure water (just deprived of air by air-pump) being added to all of a cubic inch of the new gas, over mercury: after agitation for some time, the gas diminished to be which, on examination, burned with a bright flame, and spontaneously exploded in chlorine. The aqueous solution of the gas, appeared to have no peculiar smell or taste, and did not affect litmus paper. On heating it over mercury, the gas was again expelled apparently unaltered.—Hence, I think I may venture to conclude, that pure water, recently deprived of air by the air-pump, will, at the above temperature and pressure, absorb about its own bulk of the gas, and that the gas may be again expelled, unaltered by heat.

The new gas is slowly absorbed by strong sulphuric acid, which, gradually acquires a yellowish or brownish colour, like that of a mixture of alcohol and sulphuric acid.

I have not ascertained the density of the new gas by experiment, never having had a quantity sufficient for that purpose at any one time; but from calculations founded on experiments made on its composition, which are given in the sequel; I estimate its density, (the barometer being at 30°, and thermometer at 60°,) as 0.917; atmospheric air being 1.000; and 100 cubic inches should weigh 28.4378 grains.

The new gas is gradually decomposed, when a series of electrical sparks, or discharges from a Leyden phial are passed through it; and there is a copious deposition of carbon, but no expansion, and scarcely any alteration of volume.

COMPOSITION OF THE NEW GAS.

Satisfactory evidences that the new gas is a compound of carbon and hydrogen, were gained, by firing a mixture of it with three or four times its volume of pure oxygen gas, over dry mercury; when the only products were carbonic acid gas and water. Also, by passing a series of electrical sparks, or discharges from a Leyden phial, through the new gas; when there was a copious deposition of

carbon, and inflammable air* remained. I made many experiments to determine the exact composition of the new gas, using different methods; as firing it with oxygen or nitrous gas, or employing electricity alone; but the most satisfactory results I have obtained, were, by detonating a mixture of it with rather more than four, and five times its volume of pure oxygen, over dry mercury. This experiment, requires to be made with very limited quantities of the new gas, from the violence of the explosion. The necessity of operating on small portions of the gas, was a fortunate circumstance; as I have rarely had at my disposal, at any one time, more than a single cubic inch of it; and in general, a quantity scarcely exceeding the one-fifth of that volume. In one experiment, in which I fired a mixture of five measurest of the new gas, with twelve of oxygen, the residual gas burned with a pale blue flame, showing that the oxygen was not in sufficient quantity for the consumption of that gas. In a number of other experiments, I used the oxygen in larger proportion, but I did not obtain uniform results; owing, I conceive, to the impurity of the new gas, arising chiefly from admixture with a little hydrogen, occasionally liberated from minute portions of potassium, diffused through the black substance. In a few cases, the results agreed so exactly, that I shall venture to deduce the composition of the new gas, chiefly, from two experiments.

First Experiment.

4 measures of new gas, mixed with

17 of oxygen, diminished by electricity to

15 and by agitation in a solution of potash, to

7 which were oxygen.

Second Experiment.

3 measures of new gas, mixed with

of oxygen, diminished by electricity to 16

141 and by agitation in limewater, to

 $8\frac{1}{2}$ which were oxygen.

- * Since this paper was read, I have ascertained, that the "inflammable air," here spoken of, is in fact, another new compound of carbon and hydrogen. A brief account of it was read at the last meeting of the "British Association for the Advancement of Science," held at Liverpool in 1837.
- † The measures, here and subsequently noticed, were, each of them, equivalent to about seventythree grains of mercury.

Now, as in each of the preceding experiments, all the new gas disappeared, together with one-half of its volume of oxygen; and there was produced, a volume of carbonic acid gas, exactly double the bulk of the new gas employed; it seems obvious, that the diminution arose from the union of the hydrogen of the new gas, with half its volume of oxygen; and that its carbon required for consumption twice its volume of oxygen. I therefore conclude, that one volume of the new gas, requires for its complete combustion, two and a half volumes of oxygen; of which, half a volume unites with its hydrogen, to form water, and the remaining two volumes, with its carbon, forming carbonic acid gas. Hence, the new gas appears to consist of one volume of hydrogen, and two volumes of the vapour of carbon, condensed into one volume; and 100 cubic inches of it should weigh, 28.4378 grains, and contain,—

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100 cubic inches of hydrogen, (ther. 60°, bar. 30°,)
200 cubic inches of vapour of carbon,
26.3060
Weight of 100 cubic inches of new gas,
28.4378
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The density of the new gas, should be 0.917 (estimating the weight of 100 cubic inches of atmospheric air, at 31.0117,) for 31.0117: 28.4378::1.000:0.917.

The above weights of hydrogen and carbon, are nearly in the ratio of

So that the equivalent of the new gas is 13.24; the formula by which it is expressed is 2c + H, or $c^2 + H$; and the name I shall venture to propose for it is *Bicarburet of Hydrogen*, which simply expresses its chemical constitution.

Additional evidence, that the carbon in one volume of bicarburet of hydrogen, requires two volumes of oxygen to convert it into carbonic acid gas, was obtained, by firing a mixture of four measures of it, with twenty-two measures of nitrous gas; when eight measures of carbonic acid gas were produced.

The effects of chlorine and also of electricity on the bicarburet of hydrogen, tend to confirm the fact, that it contains only its own volume of hydrogen. In the spontaneous mutual action of chlorine and bicarburet of hydrogen, these gases appear merely to condense each other in about equal volumes; forming

muriatic acid gas, whilst the carbon of the *bicarburet* is liberated. Effects, which, as is well known, are analogous to the action of hydrogen and chlorine on each other, by electricity, or the solar rays. To notice a single experiment,—

Experiment.

 $\frac{20}{100}$ cubic inch of chlorine, containing $\frac{1}{100}$ impurity, being let up into a graduated tube containing $\frac{7}{100}$ cubic inches of bicarburet of hydrogen, instant inflammation, and a copious deposition of carbon, took place; and $\frac{10}{100}$ cubic inches were condensed. Now $\frac{7}{100}$ of the gas $+\frac{7}{100}$ of chlorine $=\frac{14}{100}$ muriatic acid gas; and it was found by experiment, that upwards of $\frac{4}{100}$ of chlorine must have been absorbed, in being let up through the column of water in the tube. These results agree as nearly as can be expected, in experiments of this sort.

Electricity occasions no expansion in the bicarburet of hydrogen; for after several hundred discharges of a Leyden phial were passed through it, and it was resolved into carbon and inflammable air, there was not the slightest increase of volume; on the contrary, there was a diminution of bulk, amounting to about one-tenth of the original gas, which I am inclined to refer to the admixture of a little common air.

From comparative experiments I made on the different hydrocarbonates, I am satisfied that the bicarburet of hydrogen, is more readily decomposed by electricity than olefiant gas, and this gas more easily than carburetted hydrogen.* Thus, after passing a thousand discharges from a moderate sized Leyden phial, through about one-tenth of a cubic inch of olefiant gas in a detonating tube, the gas was only partially decomposed; for there was merely a faint partial blush of black carbonaceous matter on the surface of the tube, nearest to the wires, and an expansion not exceeding one-half of the original volume. The same number of discharges being passed through an equal bulk of carburetted hydrogen, produced on the tube, only a small quantity of a dark brownish carbonaceous substance; and an expansion not exceeding one-third of the original bulk.—

^{*} In the able work of the late Dr. Turner, "Elements of Chemistry," fifth edition, it is said, "light carburetted hydrogen is not decomposed by electricity;" but this statement is opposed to the experience of the late Sir H. Davy, and also to my own.

—Whereas, after about one-fourth of the preceding number of discharges, were passed through an equal quantity of bicarburet of hydrogen; the tube was quite obscured by a blackish crust of carbon deposited on it, but there was only a very slight contraction of the original volume of the gas.

In another experiment, made in a tube, in which the wires were placed three times farther from each other, than in the tube used in the preceding experiments; and a very large Leyden phial was employed; the first strong discharge through the bicarburet of hydrogen, occasioned a considerable deposition of carbon, on the platina wires and tubes; and a half dozen similar discharges, greatly increased such deposition, but there was no change of volume in the gas. On similar discharges being passed, separately, through olefiant and carburetted hydrogen gases, no apparent effect, in either case, took place.

I made some experiments, with a view to ascertain whether I could make the bicarburet of hydrogen combine with an additional quantity of hydrogen.—Thus, I mixed those two gases in nearly equal volumes over dry mercury, there was no immediate effect, nor any change after they had been in contact about fifteen minutes. On letting up a globule of the mixed gases into a small glass of chlorine, a loud explosion took place, and carbon was deposited. Through a part of the above mixture, I passed about a dozen discharges from a small Leyden phial, but there was no apparent change; on letting up a globule of chlorine, inflammation instantly took place, and a second globule of chlorine produced a similar effect, with deposition of carbon in both instances. The mixture of the bicarburet of hydrogen and hydrogen, burned with a dense bright flame.

The bicarburet of hydrogen, appears to offer an exception to the principle established by the able researches of the late Dr. Henry, on the then known æriform compounds of charcoal and hydrogen; namely, "that the fitness of those gases for artificial illumination is greater, as they require for combustion a greater proportional volume of oxygen;" for that gas, requires less oxygen for its combustion than olefiant gas, yet it illuminates much more powerfully than this gas. The superior illuminating power of the bicarburet of hydrogen is in strict conformity with the principle, that the degree of light emitted by the carburets of hydrogen, is dependent on the quantity of carbon they contain; the

^{*} Phil. Trans. Royal Society, 1808 and 1821.

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bicarburet of hydrogen, therefore, ought to afford more light than olefant gas, for it contains a greater relative proportion of carbon than this gas. The bicarburet of hydrogen contains $2c + \mu$; olefant gas $2c + 2\mu$; hence, the effect of the additional proportion of hydrogen in olefant gas, seems to be to diminish its illuminating power.